THERMAL DIFFUSION IN THE SEPARATION OF GAS MIXTURES

BY
BORIS LEAF
B.S. in Chem., University of Washington, 1939

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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Introduction

The development of the kinetic theory for non-uniform gas mixtures which first predicted the phenomenon of thermal diffusion has led to equations giving values of the thermal diffusion constant for gas mixtures whose molecules correspond to certain simple models, such as rigid elastic spheres, point centers of force which repel each other as inverse powers of their separation, etc.[1] Methods have also been proposed for calculating the thermal diffusion constant from the steady state concentrations obtained in the thermal diffusion column.[2] It is the purpose of this work to investigate experimentally, with a thermal diffusion column, various gas pairs, and to observe what correspondence there may be between the results obtained by application of the theory of the column to our data, and the predictions of the kinetic theory of non-uniform gas mixtures. The importance of investigating the thermal diffusion process arises from its recent successful applications to isotope separation. The complete separations of the isotopes of chlorine[3] and of neon[4] have been effected in the thermal diffusion column.

Experimental

The thermal diffusion column was constructed of brass tubing 8′ 11½″ in length. The inner, hot tube was 1.1 cm. in outer diameter while the outer, cold tube was 2.2 cm. in inside diameter. A flange on the inner tube was clamped onto the top of the outer tube by a threaded cap which screwed onto the outer tube. The inner tube was centered by means of centering pins at the bottom. A water jacket fitted around the cold tube while the hot tube was heated by a coil of No. 22 Chromel A wire mounted on alundum tubing and enclosed in a glass sheath. Four thermocouples were placed against the hot and cold tubes with junctions soldered about 8″ from the ends of each.

The gas mixtures were prepared from purified gases. Analyses of the compositions were made by observing refractive index differences with a Rayleigh type, portable, Zeiss interferometer.[5]

Results and Discussion

The results are given in the following table.

Table I

Gas Mixture	T	p	initial composition	avg. steady state composition	
				top	bottom
N_2O - CO_2	440°K	95 cm.	51.4% N_2O	45.0	50.1
C_3H_6 - cyclo-C_3H_6	388	100	52.1% C_3H_6	51.5	52.6
	387	92	52.0	51.4	52.5
	432	80	52.0	50.9	52.4
CO_2 - C_3H_8	437	100	29.8% C_3H_8	28.8	31.0
	427	113	48.1	46.5	49.5
	428	100	59.8	58.4	61.5
	423	113	68.2	66.9	69.9
	423	100	82.0	80.6	82.5
A - C_2H_6	454	80	50.0% A	46.9	54.4
CO_2 - cyclo-C_3H_6	395	98	49.7% CO_2	50.9	48.5
	396	88	49.7	50.9	48.7

In the case of the argon-ethane mixture a steady state was never obtained even after eleven hours, but the separation continued to increase with time.

The nitrous oxide - carbon dioxide pair also did not reach a steady state in seven hours but here we observe that the nitrous oxide is disappearing throughout the column leading us to conclude that it is decomposing in the presence of the hot brass tube releasing nitrogen with a much lower refractive index. Any quantitative calculations are therefore meaningless for this pair.

From the steady state values in the column, "experimental" thermal diffusion constants D_T were calculated from the theory of the column.[2] These can be compared to "theoretical"

D_T values predicted from the kinetic theory for the case of rigid elastic spheres.[1] In these calculations values for the viscosities of the gases are necessary.[6,1]

TABLE II

Gas Mixture	initial composition	D_T theoretical x 10^4	D_T experimental x 10^4
C_3H_6 - cyclo-C_3H_6	52.1% C_3H_6	4.3	1.0
	52.0	4.7	0.95
	52.0	6.7	0.91
CO_2 - C_3H_8	29.8% C_3H_8	12.8	1.3
	48.1	11.9	2.4
	59.8	12.3	2.4
	68.2	9.3	2.8
	82.0	6.8	1.6
A - C_2H_6	50.0% A	36.1	2.5
CO_2 - cyclo-C_3H_6	49.7% CO_2	0.99	1.6
	49.7	1.1	1.3

There is agreement as to order of magnitude between D_T experimental and D_T theoretical except for the argon - ethane pair which had not reached a steady state. It will be noticed that as the pressure decreases the value of D_T experimental decreases for the pairs propylene - cyclopropane and carbon dioxide - cyclopropane, while the value of D_T theoretical increases. This indicates that the pressure dependency observed using the theory of the column is incompatible with that predicted from the kinetic theory of non-uniform gases so that one of these theories must be incorrect on this point.

The rigid elastic spherical model predicts that the large and heavy molecules will accumulate at the cold wall and will therefore concentrate at the bottom of the column. From Table I we can state, therefore, that according to this model, propylene molecules are larger than cyclopropane molecules; and propane and cyclopropane molecules, larger than carbon dioxide molecules. These conclusions agree with molecular diameters calculated from viscosity data.

The behavior of the pair carbon dioxide - cyclopropane is

of especial interest because in this case the lighter molecules concentrated at the bottom and the heavier ones at the top of the column. The larger size of the cyclopropane molecules brought them to the bottom in spite of their smaller mass. This is in agreement with the behavior expected on the basis of kinetic theory and the sizes obtained from viscosity data.

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Vita

The author was born in Yokohama, Japan, on March 4, 1919. He arrived in the United States in 1922 where he has lived to this date and acquired citizenship. His early education was received in the public schools of Seattle, Washington and in 1935 he was graduated from Roosevelt High School in Seattle. He attended the University of Washington from 1935 to 1939, graduating at the end of that time with the degree of Bachelor of Science in Chemicals, summa cum laude. In the fall of 1939 he entered the graduate school of the University of Illinois with a university scholarship. The following year he held the Carr fellowship, and during 1941-42 he was a university fellow. He is a member of Phi Beta Kappa, Sigma Xi, Phi Lambda Upsilon, Pi Mu Epsilon, and Phi Kappa Phi.

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